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Mechanical Properties and Oxidation and Corrosion Resistance of Reduced- Chromium 304 Stainless Steel Alloys

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SUMMARY

An experimental program was undertaken at the NASA Lewis Research Center to identify effective substitutes for part of the chromium (Cr) in 304 stainless steel as a method of conserving the strategic element Cr. A Cr level of 12 percent was present in most of the experimental alloys evaluated rather than the normal 18 percent contained in 304 stainless steel. Substitutes for Cr in the experimental alloys included aluminum (Al), molybdenum (Mo), silicon (Si), titanium (Ti), and vanadium (V). In addition, nickel (Ni) and manganese (Mn) contents were increased over their normal concentrations in 304 stainless steel in order to achieve an austenitic structure in the reduced Cr alloys.

Results showed that the yield stress of several experimental, austenitic 12 percent Cr alloys compared favorably in magnitude and temperature dependence with the yield stress of 304 stainless steel over the temperature range of -196° to 540° C. The room temperature yield stress of the 20 experimental alloys that were investigated could be correlated with the volume fraction of austenite in the alloys. Yield stress was shown to increase linearly with decreasing austenite content. The presence of the body centered cubic martensitic or ferritic phases resulted in higher yield stresses for the alloys and influenced the resulting yield stress more than the specific Cr alloy substitutes. The cyclic oxidation resistance at 870° C for these austenitic alloys was comparable to that of 304 stainless steel. Additions of Al, Si, and Ti contributed to oxidation resistance along with the 12 percent Cr remaining in the experimental alloys. Based on corrosion measurements, the experimental 12 percent Cr alloys possess ease of passivation in H_2SO_4 and HCl environments that is comparable to that of 304 stainless steel based on anodic polarization measurements. The corrosion resistance of experimental 12 percent Cr alloys in a copper-rich H_2SO_4 - CuSO_4 solution was comparable to the corrosion resistance of 304 stainless steel; however, in a boiling HNO_3 solution, 304 stainless steel was superior to the experimental alloys. The alloy substitutes Mo, Si, and Ni were shown to be the most effective substitutes for Cr in imparting corrosion resistance.

INTRODUCTION

There continues to be strong interest in the conservation of strategic materials such as chromium (Cr). In a recent technology forecast by Metal Progress (ref. 1), emphasis was placed on the potential Cr shortage that may be imminent. It also was suggested that the Cr situation could be far more serious than the current cobalt (Co) situation. The NASA Lewis Research Center has supported both contract efforts and in-house research to investigate methods of conserving Cr for metallurgical applications. A contract effort by Crucible Materials Research Center (ref. 2) investigated cladding the inside and outside diameters of carbon steel tubing with 304 stainless steel (304SS). Results showed that a gas pressure bonding process for tube fabrication offered the feasibility of conserving about 60 percent of the Cr required to produce similar monolithic stainless steel tubing.

Research also has been underway at Lewis to demonstrate the feasibility of developing an austenitic stainless steel with reduced Cr content while maintaining the comparable corrosion and oxidation resistance exhibited by the widely used 304SS. Initial results

by Stephens and Barrett (refs. 3 and 4) showed that molybdenum (Mo) and silicon (Si) were effective substitutes for Cr for corrosion resistance while aluminum (Al) and Si were effective substitutes for high temperature (870° C) oxidation resistance. The minimum amount of Cr required in these first generation alloys to maintain good corrosion and oxidation resistance was 12 percent. These alloys possessed a ferritic or martensitic structure. Subsequent research was aimed at optimizing the composition of the alloys for corrosion and oxidation resistance and achieving an austenitic structure as is typical of 304SS. Results showed that these goals could be reached by increasing the nickel (Ni) and/or manganese (Mn) contents of the alloys and by proper balance of the Mo, Si, and Al contents (ref. 5 and unpublished data by Stephens, Barrett, and Chen on the corrosion-oxidation behavior of stainless steels on reduced chromium content). Anodic polarization corrosion tests in H₂SO₄ and HCl solutions showed that the experimental alloys possessed comparable corrosion resistance to that of 304SS (ref. 6).

This report presents the mechanical properties of typical first generation martensitic or ferritic alloys and of the second generation austenitic alloys with the Cr content primarily at the 12 percent level. Additional corrosion and oxidation data will also be presented.

EXPERIMENTAL PROCEDURE

Materials

The modified composition 304SS alloys were prepared from high purity starting materials (99.9 percent purity). Table I lists the nominal and analyzed compositions of the alloys investigated herein. In addition to the standard 304SS with 18Cr¹, alloys with reduced Cr contents (as low as 8Cr) were investigated. Substitute alloy elements for a portion of the Cr deleted from the 304SS composition included Mo, Si, Al, titanium (Ti), and vanadium (V). To achieve an austenitic structure, Ni or Mn contents were increased from their normal concentrations of 8 and 1 percent, respectively. Arc-melted ingots were hot rolled at 925° C to 0.25-centimeter-thick sheet from which tensile specimens having a 2.54-centimeter gage length and a 0.64-centimeter gage width were cut. Specimens were annealed at 980° C for 3 minutes followed by helium gas quenching. Corrosion and oxidation specimens 2.3 centimeters long by 1.3 centimeters wide cut from the 0.25-centimeter-thick sheet were heat treated in a similar manner. Complete details of alloy preparation have been presented previously (ref. 4). Volume fractions of austenite f_{γ} of the annealed alloys were determined from their magnetic strengths and by X-ray diffraction; these volume fractions are listed in table I.

Evaluation

Tensile testing. - Tensile tests were conducted at three test temperatures, -196°, 23°, and 540° C. Specimens were tested at a constant crosshead speed of 1.3 millimeters per minute. The 0.2 percent offset yield stress σ_y was determined from the load-deflection curves.

Corrosion testing. - Corrosion (Huey) tests were conducted in a boiling solution of 1N HNO₃ for 240 hours with 304SS specimen as a baseline. The 304SS specimen and seven alloy specimens were tested simultaneously in the 1N HNO₃ solution. Weight change per unit area W/A was determined for the test specimens after each 48-hour interval.

¹Alloy compositions are in weight percent.

Oxidation testing. - Alloy specimens were cyclic oxidation tested for 200 hours at 870° C. The cyclic oxidation apparatus is described in detail in reference 7. Test specimens were weighed before loading into the hot zone of a static-air furnace for 1 hour and then were automatically lifted out of the furnace to cool for a minimum of 20 minutes. This cycle was repeated until the total exposure time at 870° C reached 200 hours. Specimens were removed for weighing after the first hour of exposure and, subsequently, after 15, 30, 45, 60, 75, 90, 100, 115, 130, 145, 160, 175, 190, and 200 hours.

The specimen weight data were used to calculate specific specimen weight change data as a function of time for each alloy. The procedure used to analyze the specific specimen weight change data involved the method of multiple linear regression. The change in specific specimen weight W/A with time t was fitted by least squares (ref. 8) to equation (1):

$$\frac{\Delta W}{A} = K_1^{\frac{1}{2}} t^{\frac{1}{2}} - K_2 t \pm \text{SEE} \quad (1)$$

where K_1 is an oxidation growth constant comparable to a parabolic oxidation scaling constant, K_2 an oxide spalling constant, and SEE the standard error of estimate. An overall oxidation attack parameter was calculated from the values of K_1 and K_2 using

$$K_a = K_1^{\frac{1}{2}} + 10|K_2| \quad (2)$$

The attack parameter K_a (ref. 9) was used to rank the experimental alloys; low values of K_a corresponded to good oxidation resistance.

RESULTS AND DISCUSSION

The initial phase of this program was aimed at reducing Cr in 304SS by identifying effective substitutes that would produce comparable corrosion and oxidation resistance observed in commercial 304SS. Subsequent alloy modifications were aimed at achieving an austenitic structure with accompanying mechanical properties similar to 304SS. The first generation alloys normally contained less than 0.5 volume fraction austenite and included reduced Cr 304SS alloys, Cr substitutes of Al, Mo, Si, and Ti, and combined substitutes of Al and Mo. Second generation alloys contained fractions of austenite approaching 1.0 as a result of increasing the Ni and/or Mn concentration in the modified, reduced Cr alloys. Specific alloy properties characterized in this study are outlined in the following sections.

Tensile Properties

Reduced Cr alloys. - Tensile properties of 304SS and reduced Cr alloys are summarized in table II for tests conducted at -196°, 23°, and 540° C. The effects of reducing the Cr content in 304SS on yield stress is shown in figure 1. As the Cr content decreases, the yield stress of the alloys increases. This is opposite to the more normal alloying effect of increase in yield stress with increase in solute content. The austenite content of the alloys is listed in table I for 304SS and the experimental alloys. As the Cr content decreases, the austenite content decreases with the alloy becoming more martensitic as indicated in the constitution (Shaeffler) diagram for Ni-Cr stainless steel shown in figure 2. This increase

in martensite content, or body centered cubic (bcc) phase, is believed to be responsible for the increase in the yield stress of the reduced Cr alloys. The temperature dependence of the yield stress also is noted to be greater for the martensitic 12Cr and 8Cr alloys than for the austenitic, face centered cubic (fcc) 304SS. This characteristic is generally noted for bcc alloys compared to fcc alloys. Accompanying the increase in yield stress of the reduced Cr alloys is a marked reduction in tensile ductility as indicated in table II.

Al, Mo, Si, or Ti substitutes. - It was shown previously (ref. 4) that about 12Cr is needed in a modified alloy to achieve comparable corrosion and oxidation resistance to 304SS. Based on corrosion and cyclic oxidation studies (refs. 3 and 4), Al, Mo, Si, and Ti were identified as promising additions at the 12Cr level. The effects of adding 2 percent of each of these elements on yield stress of a 12Cr modified 304SS alloy are shown in figure 3. These alloy additions had only a minor effect on the yield stress of the 12Cr alloy. Some strengthening was produced by Al and Mo at all three test temperatures, while Si and Ti produced minimal strengthening only at 540° C. Table I indicates that these alloys contained less than 0.5 volume fraction austenite, comparable to the 12Cr base alloy.

Combined Al and Mo substitutes. - Previous results showed that combining Al and Mo in a 12Cr modified 304SS alloy produced corrosion and oxidation resistance comparable to commercial 304SS (refs. 3 and 4). The effects of these combined elements on tensile properties are summarized in table II, and yield stress data are shown in figure 4. Yield stress of the 8Cr-2Al-4Mo is the highest of any of the alloys reported herein. Combining 2Al and 2Mo at the 12Cr level produced substantial strengthening at 540° C compared to the 12Cr base alloy. Surprisingly, the yield stress data of the 12Cr-2Al-4Mo alloy approached that observed for 304SS and is considerably lower than the data for the 12Cr-2Al-2Mo alloy. In addition, tensile ductility (table II) was superior for the 12Cr-2Al-4Mo alloy compared to the other 8Cr and 12Cr alloys shown in figure 4. Table I reveals that the austenite volume fraction was 0.72 for the 12Cr-2Al-4Mo alloy compared to only 0.46 for the 12Cr-2Al-2Mo alloy. This result is unexpected since Mo is normally a ferrite stabilizer (fig. 2) and the Cr equivalent for Al has been reported to be as high as 5.5 times the Al content (ref. 10). Based on individual Cr equivalents, the 12Cr-2Al-4Mo alloy would be expected to contain a high ferrite content. The current results suggest that combined Al and Mo effects on ferrite content may not be additive.

Combined Al, Mo, Mn, and Ni substitutes. - The effects on yield stress of increasing the Ni content from 8 to 10 percent in 8Cr-2Al-2Mo or 12Cr-2Al-2Mo alloys is shown in figure 5. At the 8Cr level, this small increase in Ni content had a minor effect on yield stress. However, for the 12Cr level, the yield stress determined was essentially identical to 304SS at -196° and 23° C with some increase in yield stress noted at 540° C. Tensile elongation for the 12Cr-10Ni-2Al-2Mo alloy (table II), although not as high as for 304SS, was superior to any of the other Al-Mo modified alloys shown in figures 4 and 5. The austenite volume fraction was 0.94 for the 12Cr-10Ni-2Al-2Mo alloy.

In addition to increasing the Ni content, the effects on yield stress of simultaneously increasing Mn content from 1 to 2 or 5 percent are shown in figure 6. Yield stress data for both increased Mn content alloys are comparable to the data for 304SS. Table II shows that tensile elongations are quite similar to those values recorded for 304SS. In addition, it should be noted that these reduced Cr alloys have volume fractions of austenite of 0.99, similar to 304SS (table I).

Combined Ni, Mo, Si, and Ti substitutes. - Yield stress properties of 12Cr-10Ni-Si-Mo-Ti alloys are shown in figure 7 to be comparable to data for 304SS. In the absence of a Si increase, the 12Cr-10Ni-2Mo-2Ti alloy exhibited yield stresses higher than the 12Cr modified 304SS alloy. The volume fraction of austenite for this alloy was 0.67 compared to 0.99 for the two alloys with 1.7 and 2.7 percent Si.

Combined V, Al, Si, and Ni substitutes. - A final series of alloys was prepared which contained V as a partial substitute for Cr. Although initial results showed V to offer potential as a Cr substitute for corrosion resistance, oxidation resistance was poor. Therefore, V was combined with Al or Si to achieve better oxidation resistance in the alloy. Tensile properties are summarized in table II for this alloy series and yield stress data are shown in figure 8. The 12Cr-10Ni-2.7Si-2V alloy exhibits yield stress data similar to 304SS and contains 0.99 volume fraction of austenite. The two V alloys combined with Al had very low austenite contents and exhibited higher yield stresses.

Correlation of yield stress with austenite content. - One of the primary purposes for the second generation alloys was to achieve an austenitic, reduced Cr 304SS with comparable yield stress and tensile ductility to that of the commercial 304SS alloy. Results showed that those alloys possessing high volume fractions of austenite (0.9) exhibited yield stresses that were very similar to 304SS. The relation between the 23° C yield stress of the alloys investigated herein and their austenite volume fractions is shown in figure 9. Yield stress σ_y can be correlated with volume fraction of austenite in the alloy f_y by

$$\sigma_y (\text{in GPa}) = -1.06 f_y + 1.35 \text{ GPa}$$

The results indicate that yield stress of these reduced Cr 304SS alloys is primarily dependent on volume fraction of austenite present and not on specific alloy substitutes for Cr. The presence of the bcc martensite or ferrite phases in the alloys produces strengthening even when total solute content in the Fe-base alloy is less than that found in commercial 304SS.

Comparison with 304 stainless steel. - Those alloys with an austenite content of 0.99 exhibited room temperature yield stresses comparable to 304SS. In addition, the temperature dependence of yield stress for these austenitic alloys was comparable to that of 304SS. The following alloys fell into this category: 12Cr-10Ni-2Mn-2Al-2Mo, 12Cr-10Ni-5Mn-2Al-2Mo, 12Cr-10Ni-1.7Si-2Mo-2Ti, 12Cr-10Ni-2.7Si-1Mo-1Ti, and 12Cr-10Ni-2.7Si-2V. Room temperature (23° C) tensile ductility ranged from 38 to 70 percent for these alloys compared to 70 percent elongation for 304SS. Ductility was lower at -196° and 540° C in agreement with the trend exhibited by 304SS. The experimental alloys had somewhat lower ductilities at -196° and 540° C than did 304SS.

Oxidation Resistance

The effects of reducing Cr content in 304SS alloys and of individual alloy substitutes on cyclic oxidation resistance at 870° C has been presented previously (ref. 4). As expected, reducing Cr substantially reduced oxidation resistance. At a 12Cr level, Si and Al-Mo substitutes were shown to be effective substitutes for Cr with Ti being slightly less effective. These alloys had low volume fractions of austenite at the 12Cr-8Ni concentrations. The cyclic oxidation test results of second generation alloys, with increased Ni and Mn contents to achieve a more austenitic structure, are presented herein along with some of the earlier data of the lower austenite content alloys for comparative purposes.

Combined Al, Mo, Mn, and Ni substitutes. - The effects on cyclic oxidation resistance of combined Al-Mo substitutes for Cr are shown in figure 10 and table II. Results show that the low-austenite 12Cr-8Ni-2Al-2Mo alloy has superior oxidation resistance to the austenitic 304SS alloy. The austenitic 12Cr-10Ni-2Al-2Mo alloy exhibits rapid weight loss with oxidation time. As the Mn content is increased from 1 percent to higher concentrations in the austenitic alloys, the oxidation resistance improves. At a 5Mn content, the oxidation resistance is comparable to the lower portion of the data band shown for 11 tests conducted on commercial 304SS alloys.

Combined Ni, Mo, Si, and Ti substitutes. - Figure 11 shows the cyclic oxidation resistance of low-austenite and austenitic alloys containing Mo-Ti and Si-Mo-Ti substitutes for Cr. The low-austenite 12Cr-10Ni-2Mo-2Ti alloy has excellent oxidation resistance exhibiting a slight weight gain for the total 200 hours of testing. The austenitic alloy with 1.7Si-2Mo-2Ti is comparable to the lower portion of the data band for the commercial 304SS alloy. The austenitic 2.7Si-1Mo-1Ti alloy exhibits superior oxidation resistance to that of the commercial 304SS. A slight weight gain is noted for up to 175 hours of testing with a moderate weight loss after 200 hours.

Combined V, Al, Si, and Ni substitutes. - Oxidation resistance of V containing alloys is shown in figure 12. The low-austenite 12Cr-2Al-2V alloy exhibits essentially no change in weight throughout 200 hours of cyclic oxidation testing. Even at an 8Cr level, the weight loss is not too severe. The austenitic 12Cr-10Ni-2.75Si-2V alloy exhibits linear weight loss with cyclic oxidation time with total weight loss slightly greater than 304SS after 200 hours of testing.

Oxidation attack parameter K_a . - The attack parameter K_a was calculated for each of the experimental alloys, and values are summarized in table II. The average value of K_a for 11 tests on 304SS was 6.8. Results listed in table II indicate that as Cr is removed from 304SS K_a increases, reaching a value of 31.7 at an 8Cr level. Based on the K_a value, Si was the most effective substitute for Cr at the 12Cr level where K_a was equal to 3.8. The better austenitic alloys exhibited values of K_a ranging from 0.5 for the 12Cr-10Ni-2.7Si-1Mo-1Ti alloy to 10.5 for the 12Cr-10Ni-5Mn-2Al-2Mo alloy.

Identification of oxide scales. - X-ray diffraction data were obtained from the retained surface oxides and from the collected spall. Major oxides forming at 870° C on the basically Fe-Cr-Ni alloys are Fe_2O_3 or sesquioxides between Fe_2O_3 and Cr_2O_3 . The sesquioxides Fe_2O_3 and Cr_2O_3 are isomorphic and form a complex series of solid solutions making it difficult to differentiate between the two oxides. Spinel oxides were also identified with lattice parameters a_0 ranging from 8.30 to 8.45. X-ray fluorescence indicated primarily Fe and Ni in these spinel oxides, suggesting the presence of $Ni_xFe_{4-x}O_4$, for example, $NiFe_2O_4$. In addition to these major oxides, SiO_2 was determined to exist as a minor constituent in some of the oxides where 2.7Si was present in the alloy.

Comparison with 304 stainless steel. - Cyclic oxidation testing at 870° C showed that several of the austenitic, experimental alloys possessed good oxidation resistance. For example, based on the attack parameter K_a , the 12Cr-10Ni-2.7Si-1Mo-1Ti, 12Cr-10Ni-1.7Si-2Mo-2Ti, and 12Cr-10Ni-2.7Si-2V austenitic alloys are superior in cyclic oxidation resistance to 304SS. A 12Cr-10Ni-5Mn-2Al-2Mo alloy had an attack parameter of 10.5, slightly higher than the 6.8 value of 304SS. Figure 10 shows that the weight change data of this alloy fall within the data band for the 304SS alloys. It is thus concluded that all of the aforementioned alloys exhibit oxidation resistance that is comparable to 304SS. Oxidation resistance is achieved in these alloys as a result of combining Cr with the substitutes Al, Si, and Ti to form a protective oxide scale.

Corrosion Resistance

Corrosion tests were conducted previously on some of the first generation, low-austenite alloys in a Cu-rich H_2SO_4 - $CuSO_4$ solution (refs. 3 and 4). In addition, anodic polarization corrosion behavior of martensitic or ferritic and austenitic reduced Cr alloys has been studied in detail and reported previously (refs. 5 and 6 and the unpublished data of Stephens, Barrett, and Chen). This report presents corrosion data for selected reduced Cr 304SS alloys tested in HNO_3 (i.e., Huey test).

Reduced Cr alloys. - The effect of removing Cr from 304SS on HNO_3 corrosion resistance is shown in figure 13. This figure shows that the Cr content has a major effect on corrosion resistance in HNO_3 . After 240 hours of exposure, the weight loss for the 18Cr-304SS alloy was 10 milligrams per square centimeter (mg/cm^2) compared to $75 \text{ mg}/\text{cm}^2$ for a 12Cr alloy, and the loss for an 8Cr alloy was about $375 \text{ mg}/\text{cm}^2$ after only 70 hours of exposure.

Al, Mo, Si, or Ti substitutes. - The effects of selected substitutes for Cr in modified composition 304SS alloys with 12Cr present is shown in figure 14. Only the substitute Si improved the corrosion resistance of the 12Cr alloys, losing about $56 \text{ mg}/\text{cm}^2$ after a 240-hour exposure. The other 12Cr alloys with the various substitutes all lost approximately 85 to $95 \text{ mg}/\text{cm}^2$ after 240 hours in boiling HNO_3 compared to $75 \text{ mg}/\text{cm}^2$ for the 12Cr alloy and only 10 mg for 304SS.

Combined Al, Mo, Mn, and Ni substitutes. - Figure 15 shows the HNO_3 corrosion resistance of alloys with Al-Mo substituted for Cr in 12Cr 304SS alloys combined with Ni and Mn to achieve an austenitic structure. Combining Al and Mo did not improve the corrosion resistance of the 12Cr alloy. However, an increase in Ni content from the normal 8 percent level to the 10 percent level resulted in a substantial improvement in corrosion resistance. Increasing the Mn content from the normal 1 percent level to the 2 percent level in the 12Cr-10Ni-2Al-2Mo alloy did not change the corrosion resistance of this alloy. However, a further increase to a 5Mn level reduced corrosion resistance and nullified the beneficial effect of Ni in this alloy series.

Combined Ni, Mo, Si, and Ti substitutes. - The corrosion resistance of the final series of alloys investigated in a HNO_3 solution is shown in figure 16. Only the 12Cr-10Ni-2.7Si-1Mo-1Ti alloy had superior corrosion resistance to the 12Cr modified 304SS alloy. Apparently the combined additions of 2Mo-2Ti are detrimental to corrosion resistance and offset the benefit of the 10Ni in these alloys.

Comparison with 304 stainless steel. - Corrosion tests in HNO_3 showed that none of the experimental alloys investigated herein possessed corrosion resistance comparable to 304SS in boiling HNO_3 . The results did show that Ni and Si improved the corrosion resistance of the 12Cr alloys, and it is anticipated that further alloy modifications with emphasis on these two alloying elements could lead to corrosion resistance in boiling HNO_3 comparable to 304SS.

CONCLUDING REMARKS

A program has been conducted at NASA Lewis Research Center with the objective of reducing the Cr content in 304SS and still maintaining an austenitic structure in an alloy which possess comparable mechanical properties, oxidation resistance, and corrosion resistance to that of 304SS. The present report, which is one of a series written on this subject (refs. 3 to 6 and unpublished data by Stephens, Barrett, and Chen), emphasizes the mechanical properties of the modified composition alloys. In addition, oxidation and corrosion data are presented for selected alloys.

Results to date indicate that the major objectives of this program have been met. For example, a number of experimental alloys having Cr contents reduced to 12 percent offer properties comparable to those of 304SS. For the 12Cr alloys, it has been shown that the normal concentration of alloying elements in 304SS must be modified and added to in order to meet the objectives of this program. To achieve an austenitic structure, Ni content must be increased from 8 to 10 percent or Mn content from 1 to 5 percent. It was shown that alloys possessing a volume fraction of austenite near 0.99 exhibited tensile properties over the -196° to 540° C temperature range that were very similar to 304SS.

To achieve comparable cyclic oxidation resistance at high temperatures (870° C) to that of 304SS, Al and Si additions to the austenitic 12Cr alloys were required. Results of the current work and the unpublished work of Stephens, Barrett, and Chen showed that an addition of 1 percent Al or an increase of Si content from 0.7 to about 2 percent was effective in producing comparable oxidation properties to that of 304SS.

Initial corrosion testing was conducted in a Cu-rich H₂SO₄-CuSO₄ solution as a means of ranking experimental alloys (refs. 3 and 4). Several reiterations were conducted until corrosion resistance was comparable to 304SS. Subsequent anodic polarization testing in H₂SO₄ and HCl showed that experimental alloys exhibited anodic polarization behavior similar to 304SS (refs. 5 and 6 and unpublished work of Stephens, Barrett, and Chen). An addition of 1 to 2 percent Mo and an increase in Si content from 0.7 to about 2 percent were both identified as being effective in promoting passivation and anodic polarization behavior comparable to 304SS. The current work explored the corrosion resistance of selected alloys in a HNO₃ solution. The results indicated that, based on specific weight change, none of the experimental alloys were as resistant to attack as 304SS in this particular corrosion medium. Alloying elements Ni and Si were identified as effective elements in improving corrosion resistance of the 12Cr modified composition 304SS alloys. Reiterations of alloy composition will be required to produce corrosion resistance of the experimental alloys that is comparable to 304SS in HNO₃.

Based on the various studies to date, a single alloy which best meets the objectives of this program and conserves one-third of the Cr normally used in 304SS has a composition of 12Cr-10Ni-1.5Si-1Al-2Mo plus the other alloying elements found in 304SS at their normal concentration. It is anticipated that this alloy may be used for most applications where 304SS is currently used, but it may have limited use in a HNO₃ environment.

SUMMARY OF RESULTS

The following results were obtained from an experimental program to investigate the mechanical properties, oxidation resistance, and corrosion resistance of reduced Cr 304SS:

1. The yield stress of austenitic, 12Cr alloys over the -196° to 540° C temperature range compares favorably in magnitude and temperature dependence to commercial 304SS. Five experimental alloys exhibiting this behavior include the following alloy compositions: 12Cr-10Ni-2Mn-2Al-2Mo, 12Cr-10Ni-5Mn-2Al-2Mo, 12Cr-10Ni-1.7Si-2Mo-2Ti, 12Cr-10Ni-2.7Si-1Mo-1Ti, and 12Cr-10Ni-2.7Si-2V.

2. Yield stress of 20 experimental alloys with volume fraction of austenite ranging from 0.99 to 0.25 increased linearly with decreasing austenite content.

3. Based on the oxidation attack parameter K_a which takes into account parabolic growth and linear spalling, four of the five austenitic alloys just listed have cyclic oxidation resistance at 870° C comparable to 304SS. The alloy additions of Al, Si, and Ti combined with the Cr remaining in the alloys are believed to account for the oxidation resistance of these alloys.

4. Based on weight loss, corrosion resistance in boiling 1N HNO₃ of all experimental alloys was inferior to that of the commercial 304SS. Alloy additions of Ni and Si were identified as effective elements in improving corrosion resistance of the 12Cr modified composition 304SS alloys.

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Cleveland, Ohio, July 26, 1979,
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TABLE I. - CHEMICAL ANALYSIS AND AUSTENITE CONTENT OF
REDUCED Cr 304 STAINLESS STEEL ALLOYS

Alloy designation	Analyzed composition, ^a wt %								Volume fraction austenite, f_{γ}
	Cr	Ni	Mn	Si	Al	Mo	Ti	V	
Reduced Cr alloys									
18Cr (304 stainless steel) ^b	18.5	7.8	1.0	0.7	---	---	---	---	0.99
12Cr	12.3	8.8	.8	.6	---	---	---	---	.45
8Cr	8.1	6.3	1.0	.7	---	---	---	---	.41
Cr substitutes Al, Mo, Si, or Ti									
12Cr-2Al	11.5	6.8	0.8	0.6	1.9	---	---	---	0.41
12Cr-2Mo	12.1	8.1	.8	.6	---	2.0	---	---	.35
12Cr-2.7Si	12.0	7.3	.7	2.5	---	---	---	---	.46
12Cr-2Ti	11.6	7.0	.8	.6	---	---	1.9	---	.57
Combined Cr substitutes Al, Mo, Mn, and Ni									
12Cr-2Al-2Mo	12.0	8.2	0.6	0.6	2.0	2.0	---	---	0.46
12Cr-2Al-4Mo	11.9	8.0	1.0	↓	2.0	4.0	---	---	.72
8Cr-2Al-4Mo	8.1	8.1	.8		2.1	4.2	---	---	.34
12Cr-10Ni-2Al-2Mo	11.9	9.9	.9		1.9	2.0	---	---	.94
8Cr-10Ni-2Al-2Mo	9.0	10.3	1.0		2.1	2.1	---	---	.53
12Cr-10Ni-2Mn-2Al-2Mo	11.9	10.1	2.1	↓	2.1	2.2	---	---	.99
12Cr-10Ni-5Mn-2Al-2Mo	12.0	10.5	4.7		2.4	2.3	---	---	.99
Combined Cr substitutes Ni, Mo, Si, and Ti									
12Cr-2.7Si-2Mo	12.4	8.5	0.7	2.5	---	1.8	---	---	0.84
12Cr-10Ni-2Mo-2Ti	12.2	10.4	1.0	.6	---	2.0	2.0	---	.67
12Cr-10Ni-1.7Si-2Mo-2Ti	11.8	10.1	.9	1.6	---	2.1	2.0	---	.99
12Cr-10Ni-2.7Si-1Mo-1Ti	12.9	9.9	1.0	2.5	---	1.0	1.0	---	.99
Combined Cr substitutes Ni, Al, Si, and V									
12Cr-2Al-2V	12.2	8.2	0.8	0.6	2.0	---	---	1.9	0.32
8Cr-2Al-2V	12.0	8.3	.6	.6	2.0	---	---	2.0	.25
12Cr-10Ni-2.7Si-2V	11.9	10.8	1.0	2.6	---	---	---	2.3	.99

^aCarbon content, 0.05 wt % in all alloys.

^bNormal composition, Fe-18Cr-8Ni-1Mn-0.7Si-0.05C.

TABLE II. - TENSILE PROPERTIES AND OXIDATION ATTACK PARAMETER OF REDUCED
Cr 304 STAINLESS STEEL ALLOYS

Alloy designation	Yield stress, σ_Y , GPa			Ultimate stress, σ_U , GPa			Elongation, percent			Oxidation attack parameter, K_a
	Test temperature, °C									
	-196	23	540	-196	23	540	-196	23	540	
Reduced Cr alloys										
18Cr (304 stainless steel)	0.47	0.26	0.09	1.60	0.66	0.44	36	70	40	6.8
12Cr	1.28	.83	.37	1.64	1.16	.50	12	7	18	15.1
8Cr	1.32	.95	.55	1.41	1.12	.74	1	8	8	31.7
Cr substitutes Al, Mo, Si, or Ti										
12Cr-2Al	1.37	0.96	0.63	1.60	1.25	0.95	10	5	13	10.4
12Cr-2Mo	1.41	.90	.74	1.62	1.07	.83	13	9	15	20.3
12Cr-2.7Si	1.08	.63	.49	1.87	1.26	.59	20	11	24	3.8
12Cr-2Ti	1.23	.74	.60	1.47	1.01	.79	10	2	14	12.7
Combined Cr substitutes Al, Mo, Mn, and Ni										
12Cr-2Al-2Mo	1.38	0.89	0.75	2.32	1.25	0.89	16	10	11	0.6
12Cr-2Al-4Mo	.83	.43	.36	2.03	1.10	.61	17	22	20	1.3
8Cr-2Al-4Mo	1.58	1.10	.88	1.74	1.26	1.06	9	15	10	14.8
12Cr-10Ni-2Al-2Mo	.46	.26	.23	1.94	.97	.51	22	25	30	19.8
8Cr-10Ni-2Al-2Mo	1.28	.79	.85	1.68	1.23	1.14	12	4	6	13.7
12Cr-10Ni-2Mn-2Al-2Mo	.52	.26	.16	1.90	.75	.48	33	65	33	29.6
12Cr-10Ni-5Mn-2Al-2Mo	.63	.29	.16	1.70	.67	.50	50	70	38	10.5
Combined Cr substitutes Ni, Mo, Si, and Ti										
12Cr-2.7Si-2Mo	0.77	0.39	0.28	1.63	1.21	0.51	20	13	36	10.1
12Cr-10Ni-2Mo-2Ti	1.47	.98	.88	1.81	1.23	1.00	10	9	41	.2
12Cr-10Ni-1.7Si-2Mo-2Ti	.70	.43	.90	1.39	.90	.23	10	38	28	4.8
12Cr-10Ni-2.7Si-1Mo-1Ti	.35	.30	.19	2.21	1.13	.57	16	40	39	.5
Combined Cr substitutes Ni, Al, Si, and V										
12Cr-2Al-2V	1.55	1.06	0.90	1.72	1.25	1.07	10	8	11	0.05
8Cr-2Al-2V	1.31	1.01	.66	1.67	1.17	.80	19	12	15	16.9
12Cr-10Ni-2.7Si-2V	.52	.32	.22	2.17	.96	.59	24	47	35	4.2

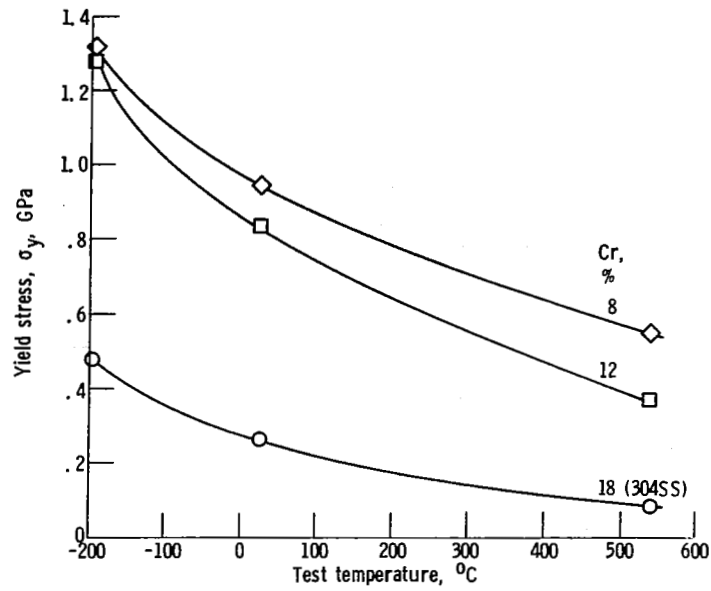


Figure 1. - Effects of temperature on yield stress of reduced Cr 304SS alloys.

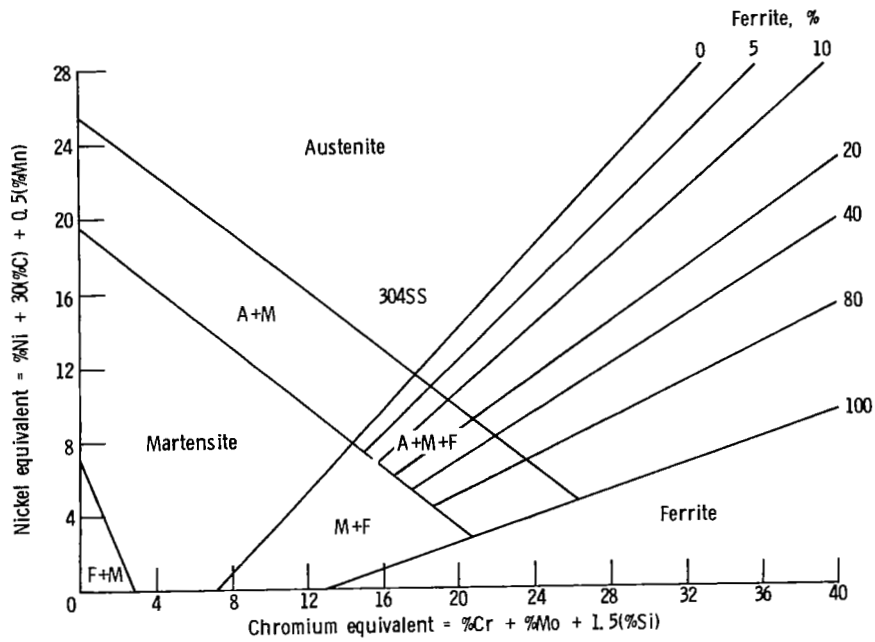


Figure 2. - Constitution (Schaeffler) diagram for Cr-Ni stainless steels.

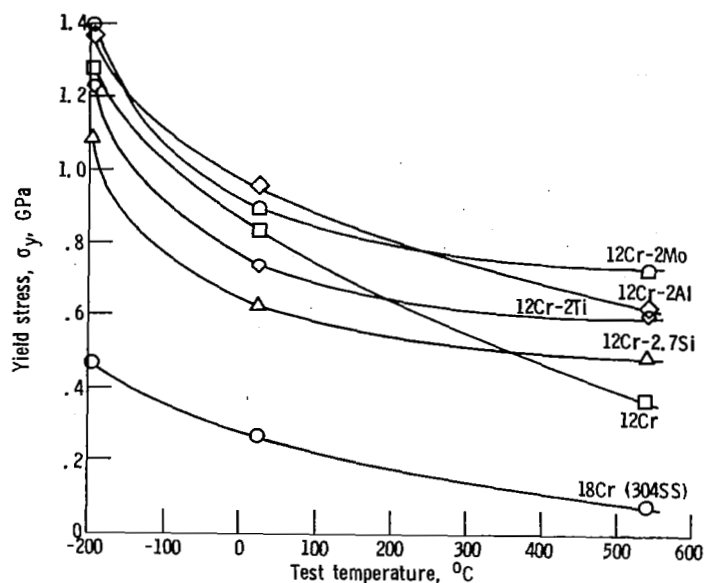


Figure 3. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing Al, Mo, Si, or Ti substitutes.

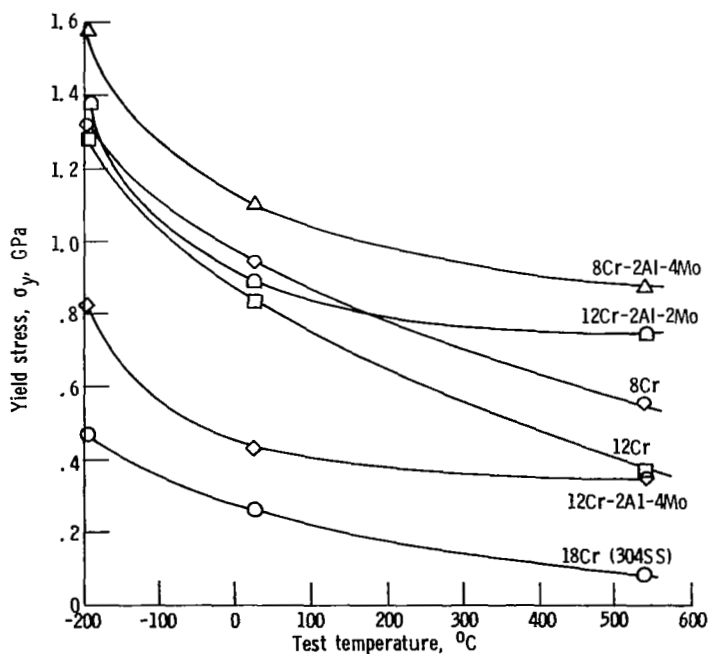


Figure 4. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing combined Al and Mo substitutes.

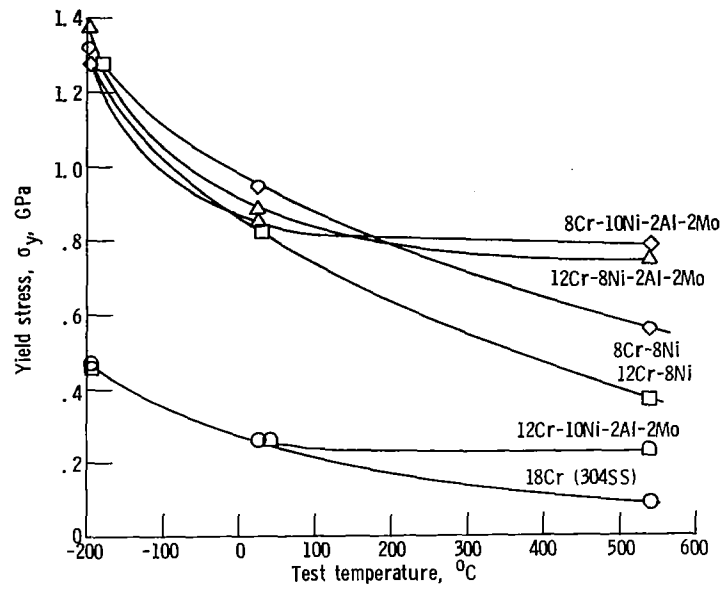


Figure 5. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing combined Ni, Al, and Mo substitutes.

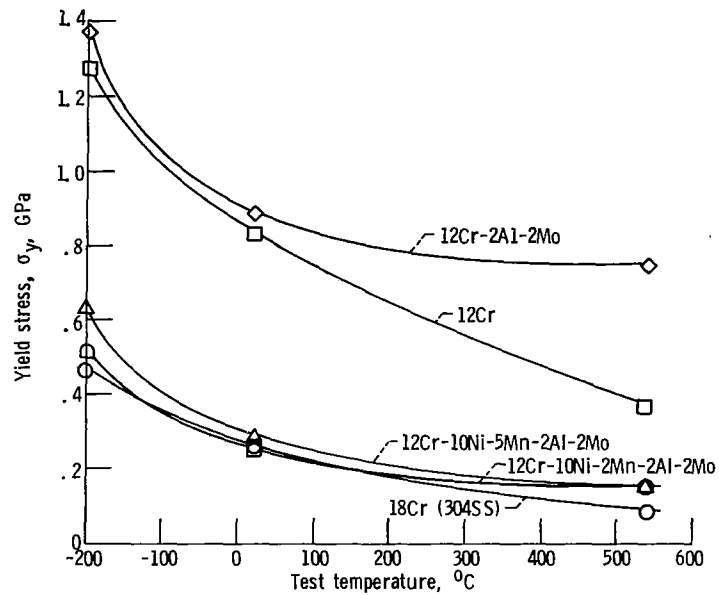


Figure 6. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing combined Ni, Mn, Al, and Mo substitutes.

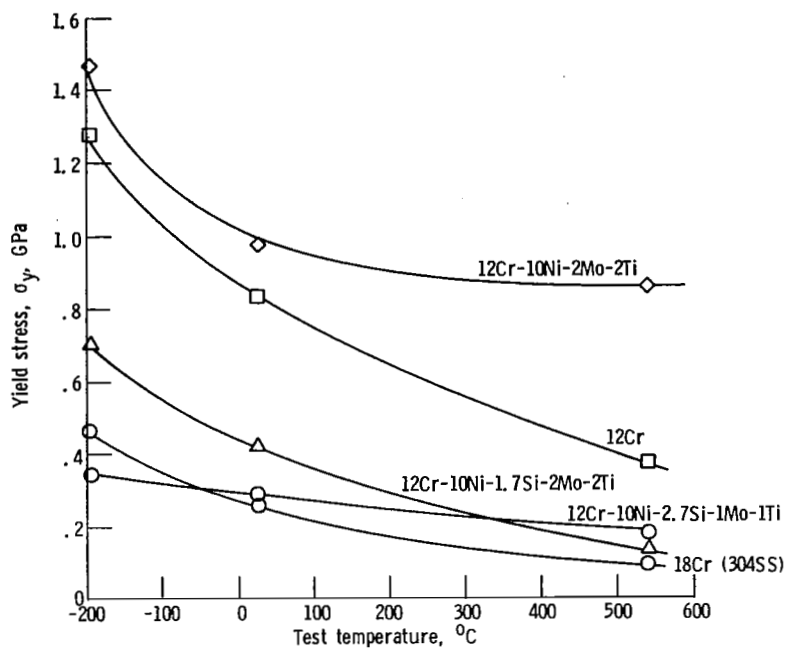


Figure 7. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing combined Ni, Si, Mo, and Ti substitutes.

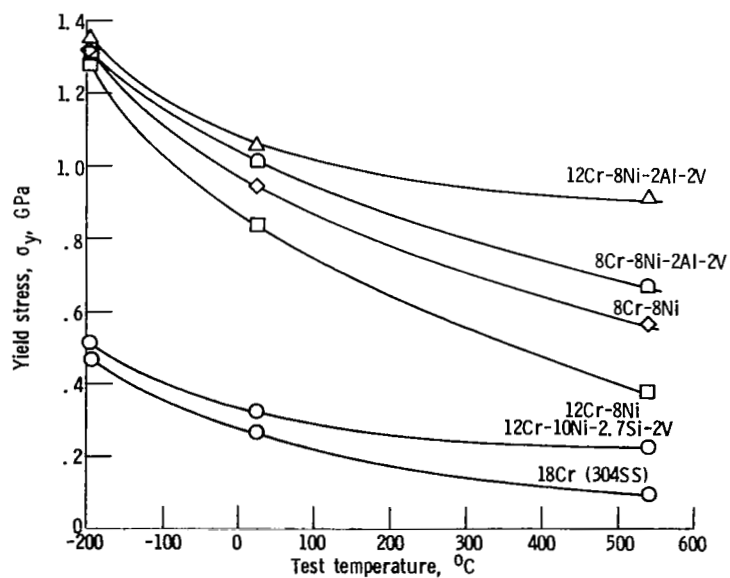


Figure 8. - Effects of temperature on yield stress of reduced Cr 304SS alloys containing combined V, Al, Si, and Ni substitutes.

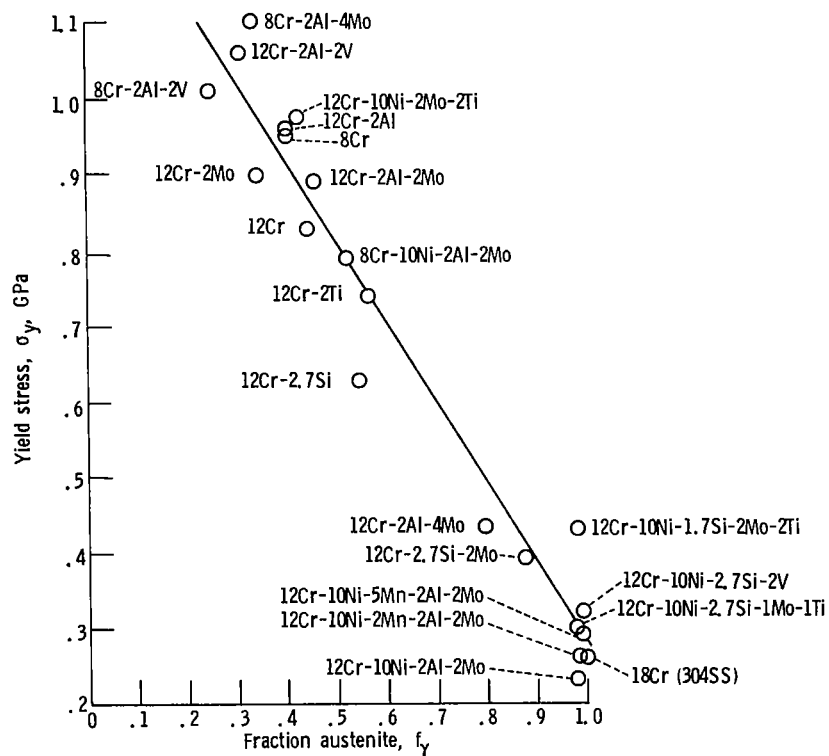


Figure 9. - Dependence of 23°C yield stress on volume fraction of austenite for reduced Cr 304SS alloys.

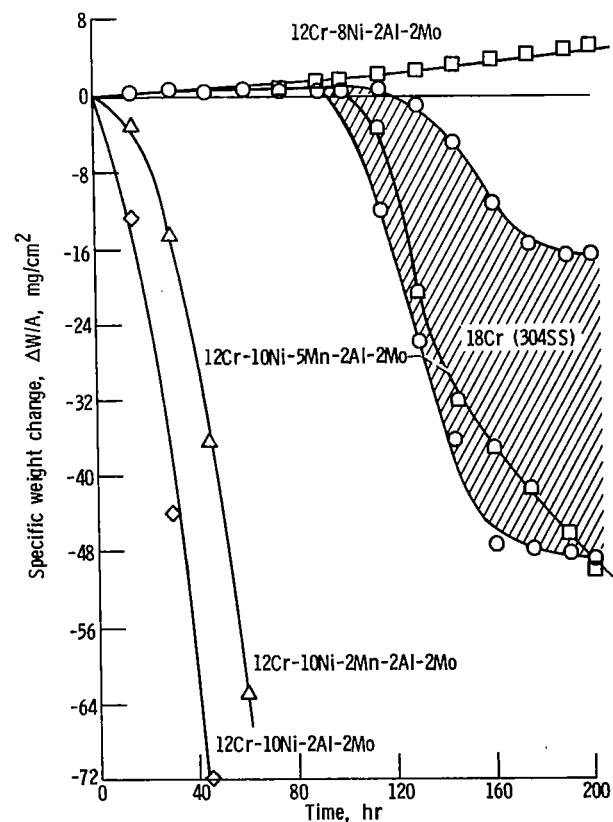


Figure 10. - Specific weight change data as function of cyclic oxidation time at 870°C for reduced Cr 304SS alloys with combined Al, Mo, Mn, and Ni substitutes.

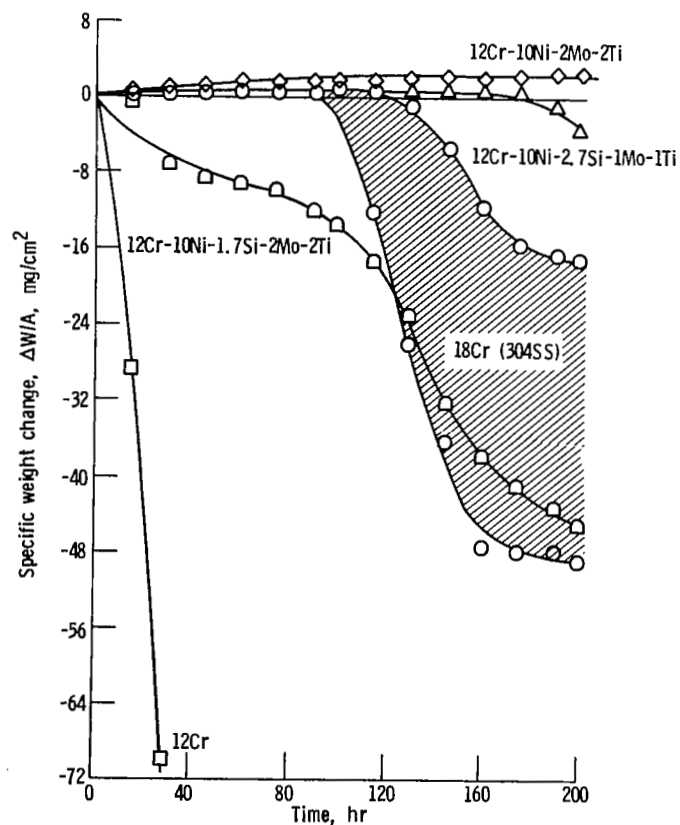


Figure 11. - Specific weight change data as function of cyclic oxidation time at 870°C for reduced Cr 304SS alloys with combined Ni, Mo, Si, and Ti substitutes.

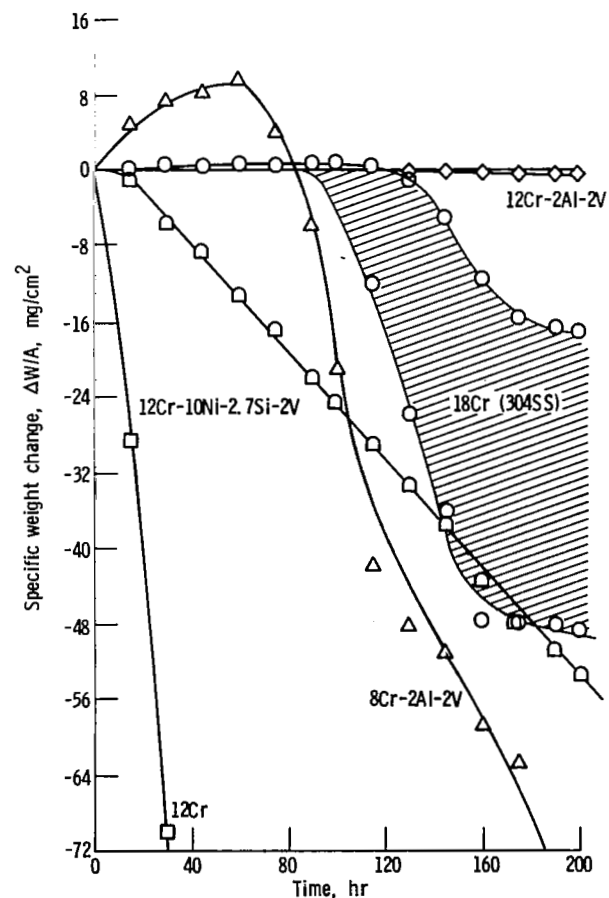


Figure 12. - Specific weight change data as function of cyclic oxidation time at 870°C for reduced Cr 304SS alloys with combined V, Al, Si, and Ni substitutes.

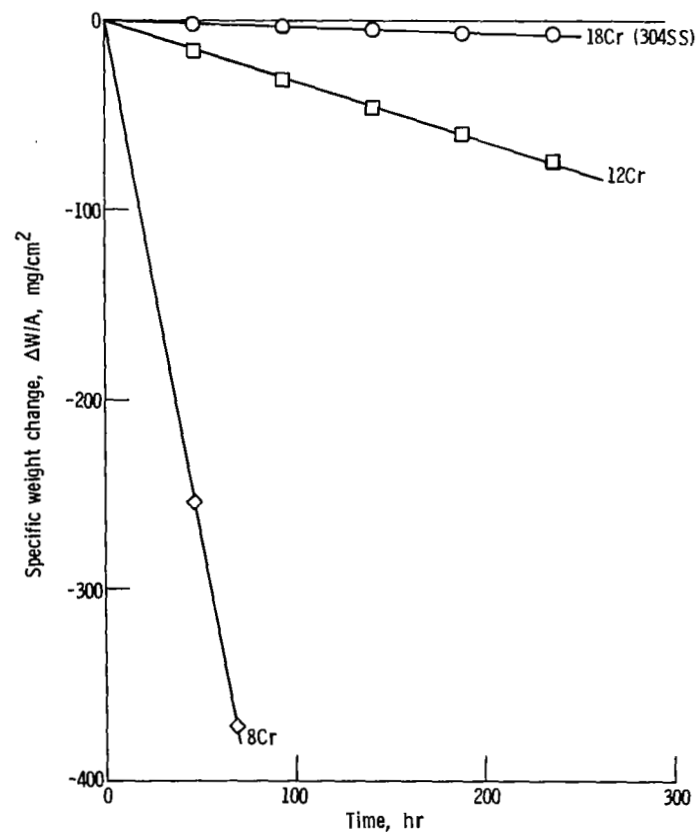


Figure 13. - Effects of HNO_3 exposure time on specific weight change data of reduced Cr 304SS alloys.

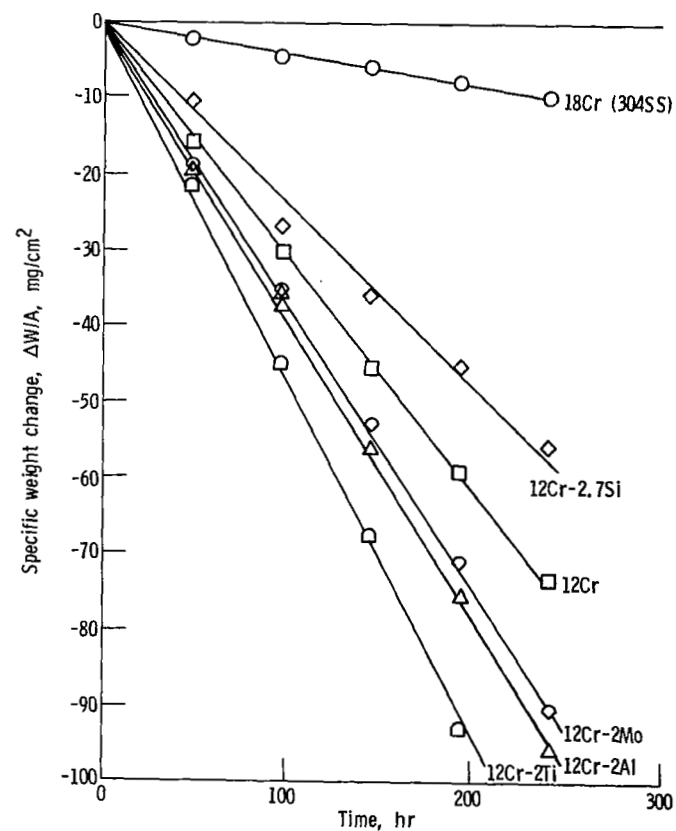


Figure 14. - Effects of HNO_3 exposure time on specific weight change data of reduced Cr 304SS alloys with Al, Mo, Si, or Ti substitutes.

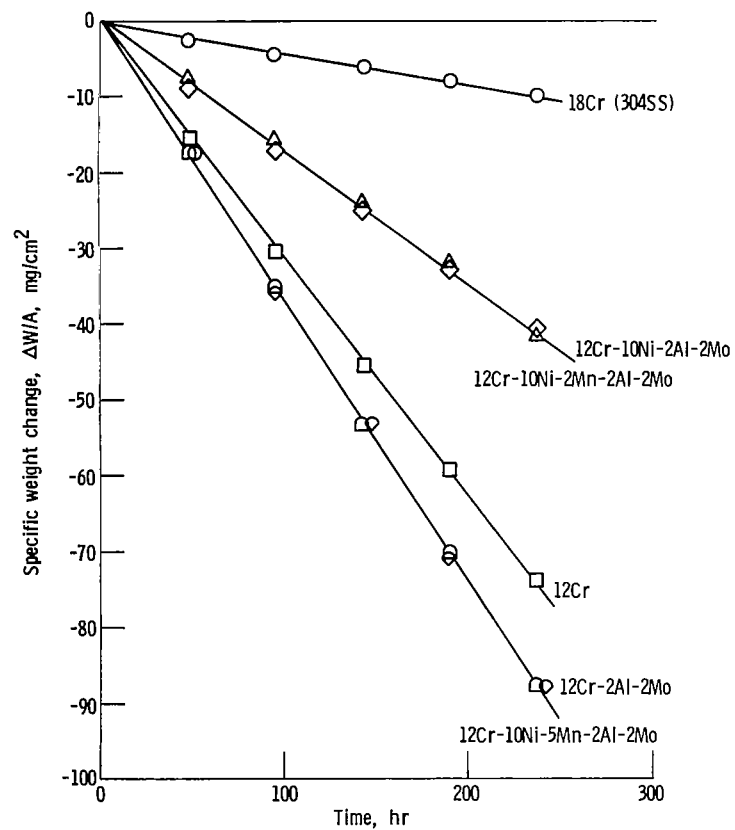


Figure 15. - Effects of HNO_3 exposure time on specific weight change data of reduced Cr 304SS alloys with Ni, Mn, Al, and Mo substitutes.

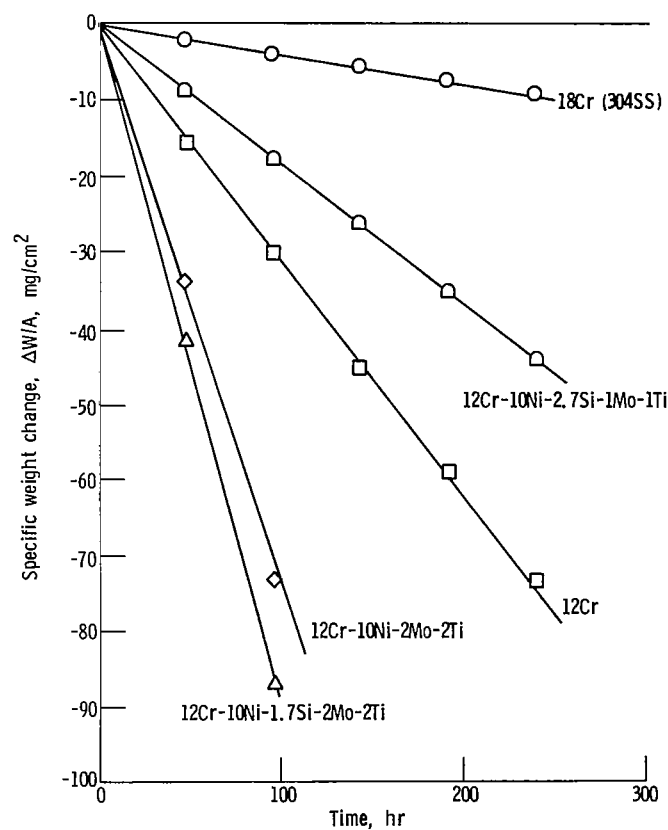


Figure 16. - Effects of HNO_3 exposure time on specific weight change data of reduced Cr 304SS alloys with Ni, Si, Mo, and Ti substitutes.

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16. Abstract <p>An experimental program was undertaken to identify effective substitutes for part of the Cr in 304 stainless steel as a method of conserving the strategic element Cr. Although special emphasis was placed on tensile properties, oxidation and corrosion resistance were also examined. Results showed that over the temperature range of -196° to 540° C the yield stress of experimental austenitic alloys with only 12 percent Cr compared favorably with the 18 percent Cr in 304 stainless steel. Oxidation resistance and in most cases corrosion resistance for the experimental alloys were comparable to the commercial alloy. Effective substitutes for Cr included Al, Mo, Si, Ti, and V, while Ni and Mn contents were increased to maintain an austenitic structure.</p>					
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